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ORGANOTHALLIUM COMPOUNDS

XVII *. HALOGENOBIS(POLYFLUOROPHENYL)THALLIUM(III) COMPLEXES

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Summary

The preparations, stabilities and structures of the complexes R_2TlX and R_2LTlX ($R = C_6F_5$, p-HC_6F_4, or o-HC_6F_4; X = Br or Cl; $L = Ph_3PO$, 2,2′-bipyridyl (bpy) or Ph_3P) have been examined or ($R = C_6F_5$) reinvestigated. The derivatives R_2TlX are monomeric in acetone, from which the complex $(p\text{-}HC_6F_4)_2Me_2COTlBr$ has been isolated. In this solvent, the complexes R_2LTlX ($L = Ph_3PO$, bpy, or Ph_3P) undergo partial dissociation by loss of L. When L = bpy, there is also slight ionization into R_2LTl^+ and $R_2TlX_2^-$. The acceptor properties of R_2TlX compounds towards uncharged ligands decrease $R = C_6F_5 \simeq p\text{-}HC_6F_4 > o\text{-}HC_6F_4 > Ph$. Dimeric behaviour is observed for R_2TlX compounds in benzene, whilst R_2LTlX ($L = Ph_3PO$ or bpy) derivatives show slight but significant association. In the solid state, R_2TlX compounds are considered to be polymeric with five coordinate thallium, and R_2LTlX derivatives to be dimeric with five ($L = Ph_3PO$) or six (L = bpy) coordinate thallium by contrast with four coordinate dimeric and four or five coordinate monomeric structures previously proposed for the respective pentafluorophenyl derivatives. Halogen bridging is unsymmetrical for $R = C_6F_5$ or p-HC_6F_4, but may be more symmetrical for $R = o\text{-}HC_6F_4$ when $L = Ph_3PO$ or bpy. Reported structural data for the complexes $(C_6F_5)_2LTlX$ ($L = Ph_3AsO$, Ph_3P, Ph_3As, or 1,10-phenanthroline; X = Br or Cl) and $(C_6F_5)_2TlCl_2^-$ are reinterpreted and the proposed structures revised.

Introduction

Several classes of halogenobis(pentafluorophenyl)thallium(III) complexes have been prepared [2,3] and a series of interrelated structures proposed mainly

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[*] Part XVI, Ref. 1.

on the basis of molecular weight and far infrared measurements [2—4]. Attempts over several years to test these proposals by crystal structures of representative compounds, e.g. $(C_6F_5)_2TlBr$ and $(C_6F_5)_2bpyTlBr$ (bpy = 2,2′-bipyridyl), have been unsuccessful (e.g. [5,6]). Recent extensions of these studies to halogenobis(2,3,5,6-tetrafluorophenyl)thallium(III) compounds [7,8] have provided crystals of $(p\text{-}HC_6F_4)_2TlBr$ and $(p\text{-}HC_6F_4)_2Ph_3POTlCl$ suitable for X-ray examination. The former is polymeric [9] and the latter dimeric [8], both with five coordinate thallium and halogen bridging. This contrasts with the four coordinate dimeric and four coordinate monomeric structures proposed [2—4] for the pentafluorophenyl analogues, and suggests that reappraisal of the structural data for these compounds is needed. In addition, the credibility of proposed structures for other halogenobis(pentafluorophenyl)thallium(III) complexes, e.g. monomeric five coordination for $(C_6F_5)_2bpyTlX$ (X = Br or Cl) [2], is called into question. In this paper, the structures and coordination chemistry of $(C_6F_5)_2TlX$, $(p\text{-}HC_6F_4)_2TlX$, and $(o\text{-}HC_6F_4)_2TlX$ compounds are compared. Data for the pentafluorophenyl compounds have been reinvestigated and reinterpreted, and structural conclusions are related to the crystal structures of $(p\text{-}HC_6F_4)_2TlBr$ [9] and $(p\text{-}HC_6F_4)_2Ph_3POTlCl$ [8].

Results and discussion

1. *Preparations*

Bromobis(polyfluorophenyl)thallium(III) compounds were prepared by reported methods [2,7,10], and were converted into the corresponding chloro-complexes by metathesis with silver chloride [see ref. 2 for $(C_6F_5)_2TlCl$]. Surprisingly, analytically pure $(p\text{-}HC_6F_4)_2TlCl$ showed sharp $\nu(OH)$ absorptions at 3647 and 3570 cm^{-1}. These cannot be attributed to an impurity of $(p\text{-}HC_6F_4)_2TlOH$ since they are not removed on treatment of the compound with hydrochloric acid under conditions (see ref. 7) suitable for neutralization of hydroxobis(polyfluorophenyl)thallium(III) compounds. Accordingly, the absorptions are attributed to the presence of water. The sharpness and high frequencies of the bands suggest the absence of hydrogen bonding [11]. Up to 0.4 mole of water per mole of complex can be accommodated without significant (>0.3%) change in the analytical figures.

The complexes $(C_6F_5)_2Ph_3POTlX$ (X = Br or Cl) [3], $(p\text{-}HC_6F_4)_2Ph_3POTlCl$ [8], and $(o\text{-}HC_6F_4)_2Ph_3POTlBr$ were readily prepared from equimolar amounts of triphenylphosphine oxide and the appropriate halogenobis(polyfluorophenyl)thallium(III) compound in aqueous methanol, and $(p\text{-}HC_6F_4)_2Ph_3POTlBr$ [8] was obtained from a similar reaction in benzene/petroleum spirit. A five fold excess of ligand was necessary for isolation of $(o\text{-}HC_6F_4)_2Ph_3POTlCl$ from aqueous methanol. The $\nu(PO)$ frequencies of the R_2Ph_3POTlX complexes (Table 1) are lowered significantly (20—40 cm^{-1}) from the free ligand value, as expected [12,13] on coordination. Attempts to prepare $(p\text{-}HC_6F_4)_2Ph_3POTlBr$ and $(o\text{-}HC_6F_4)_2Ph_3POTlCl$ from equimolar amounts of reagents in aqueous methanol gave products of composition $(p\text{-}HC_6F_4)_2(Ph_3PO)_{1.2}TlBr$ and $(o\text{-}HC_6F_4)_2(Ph_3PO)_{0.35}TlCl$ respectively. The former is not simply a mixture of triphenylphosphine oxide and $(p\text{-}HC_6F_4)_2Ph_3POTlBr$, since $\nu(PO)$ of the free ligand was not observed. In addition, the density of all crystals was greater than

TABLE 1

PHOSPHORUS—OXYGEN AND THALLIUM—HALOGEN ABSORPTION FREQUENCIES (cm^{-1}) OF HALOGENOBIS(POLYFLUOROPHENYL)THALLIUM(III) COMPOUNDS

Compound	ν(PO)	ν(Tl—X) [a] IR	δ(Tl—X) [b] IR	ν(Tl—X) [a] R
$(C_6F_5)_2TlBr$		150 [c]	68 [c]	
$(p\text{-}HC_6F_4)_2TlBr$		148	74	
$(o\text{-}HC_6F_4)_2TlBr$		151	74	
$(C_6F_5)_2TlCl$		213 [c]	133 [c]	
$(p\text{-}HC_6F_4)_2TlCl$		216	104	
$(o\text{-}HC_6F_4)_2TlCl$		181 [d]	105	
$(C_6F_5)_2Ph_3POTlBr$	1170	170 [c]	84 [c]	
$(p\text{-}HC_6F_4)_2Ph_3POTlBr$	1172	167	84	
$(p\text{-}HC_6F_4)_2(Ph_3PO)_{1.2}TlBr$	1170			
$(o\text{-}HC_6F_4)_2Ph_3POTlBr$	1158	154	84	
$(C_6F_5)_2Ph_3POTlCl$	1171	244 [c]	144 [c]	
$(p\text{-}HC_6F_4)_2Ph_3POTlCl$	1172	239	147 [d]	
$(o\text{-}HC_6F_4)_2Ph_3POTlCl$	1163, 1160	221	118 [d]	
$(o\text{-}HC_6F_4)_2(Ph_3PO)_{0.35}TlCl$	1131			
$(o\text{-}HC_6F_4)_2(Ph_3PO)_{0.55}TlCl$	1162, 1131			
$(C_6F_5)_2bpyTlBr$		161		160
$(p\text{-}HC_6F_4)_2bpyTlBr$		142 or 126 [d]		ca. 148
$(o\text{-}HC_6F_4)_2bpyTlBr$		115		145 [d]
$(C_6F_5)_2bpyTlCl$		228 or 210		240 or 210
$(p\text{-}HC_6F_4)_2bpyTlCl$		216 or 198 [d]		200
$(o\text{-}HC_6F_4)_2bpyTlCl$		132		178

[a] Complex vibration involving thallium—halogen stretching. [b] Complex vibration involving thallium—halogen bending. [c] Consistent with reported assignments [2—4]. [d] Assignment uncertain.

that of carbon tetrachloride (1.59 g cm^{-3}; cf. Ph_3PO, 1.21 g cm^{-3}). Possibly, a mixture of $(p\text{-}HC_6F_4)_2Ph_3POTlBr$ and $(p\text{-}HC_6F_4)_2(Ph_3PO)_2TlBr$ was obtained. An attempt to prepare the latter from stoichiometric amounts of the phosphine oxide and $(p\text{-}HC_6F_4)_2TlBr$ failed. The ν(PO) frequency of $(o\text{-}HC_6F_4)_2$-$(Ph_3PO)_{0.35}TlCl$ (1131 cm^{-1}) was considerably lower than that (1162 cm^{-1}) of $(o\text{-}HC_6F_4)_2Ph_3POTlCl$, precluding a mixture of the 1 : 1 complex and $(o\text{-}HC_6F_4)_2TlCl$, and indicating the presence of a distinct new species. Reaction of triphenylphosphine oxide with $(o\text{-}HC_6F_4)_2TlCl$ using a mole ratio of 2 : 1 in aqueous methanol gave a solid of composition $(o\text{-}HC_6F_4)_2(Ph_3PO)_{0.55}TlCl$, which showed ν(PO) at both 1131 and 1162 cm^{-1}. All R_2Ph_3POTlX complexes show significant absorption near 410 cm^{-1}, which may be assigned to ν(Tl—O) or to a component of the 'X-sensitive' mode *t* of the PhP group [14].

The new 2,2′-bipyridyl complexes, R_2 bpyTlX (R = $p\text{-}HC_6F_4$ or $o\text{-}HC_6F_4$; X = Br or Cl) were readily prepared by a method similar to that used for the corresponding pentafluorophenyl complexes [2]. The complex $(C_6F_5)_2Ph_3PTlBr$ was obtained from equimolar amounts of triphenylphosphine and $(C_6F_5)_2TlBr$ in aqueous methanol, by contrast with the need to use an excess of the ligand in previous preparations of $(C_6F_5)_2Ph_3PTlX$ (X = Br or Cl) complexes [3]. However, analogous syntheses of R_2Ph_3PTlBr derivatives (R = $p\text{-}HC_6F_4$ or $o\text{-}HC_6F_4$) failed, and the formation of these complexes in solution (section 3) was investigated without their isolation.

2. *Properties of the solid complexes*

X-ray powder photography shows that the complexes $(C_6F_5)_2TlX$ (X = Br or Cl) are isomorphous, but a similar relationship does not exist between the corresponding 2,3,5,6-tetrafluorophenyl compounds, presumably owing to hydration of the chloro derivative. It has previously been shown that $(C_6F_5)_2Ph_3POTlBr$ and $(C_6F_5)_2Ph_3POTlCl$ are isomorphous [3], and the 2,3,5,6-tetrafluorophenyl analogues show similar behaviour (this work).

Infrared absorptions sensitive to the mass of the halogen are listed in Table 1, though for some compounds their identification is uncertain. Analogous Raman data are given for R_2bpyTlX complexes. Designation of modes as thallium—halogen stretching or bending is convenient, but is a considerable approximation in view of the nature of the thallium—halogen bonding (section 5). Agreement with previous assignments [2—4] for pentafluorophenylthallium(III) compounds is generally satisfactory.

3. *Properties of the complexes in solution*

The complexes R_2TlX ($R = C_6F_5$ or p-HC_6F_4; X = Br or Cl) are substantially dimeric in benzene (Experimental Section). Equilibrium constants for reaction (1) are given in Table 2.

$$2\,R_2TlX \rightleftharpoons (R_2TlX)_2 \qquad (1)$$

Molecular weights could not be obtained for $(o$-$HC_6F_4)_2TlX$ derivatives in this solvent owing to solubility limitations. The R_2TlX derivatives are nonelectrolytes and monomeric ($R = C_6F_5$ or p-HC_6F_4, X = Br or Cl; $R = o$-HC_6F_4, X = Br) or very slightly associated $[(o$-$HC_6F_4)_2TlCl]$ in acetone (see Experimental). Coordination of acetone has been suggested to account for the lower association of $(C_6F_5)_2TlX$ derivatives in this solvent than in benzene, but no confirmation could be obtained by preparative experiments [2]. Extension of the study to 2,3,5,6-tetrafluorophenyl derivatives has now enabled $(p$-$HC_6F_4)_2Me_2COTlBr$ to be isolated from a solution of $(p$-$HC_6F_4)_2TlBr$ in acetone. The ν(CO) frequency of the product (1694 and/or 1678 cm^{-1}, depending on the mull used) was lowered from the free ligand value (1714 cm^{-1}), as expected [15] for coordination of acetone. The complex showed surprising thermal stability. After treatment with boiling benzene, some acetone was still retained [0.4

TABLE 2

MOLECULAR WEIGHT DATA AND EQUILIBRIUM CONSTANTS FOR HALOGENOBIS(POLYFLUOROPHENYL)THALLIUM(III) COMPLEXES IN BENZENE

Complex	Concn. [a] (mol dm^{-3})	i [b]	K_{dim} [c] (mol^{-1} dm^3)
$(C_6F_5)_2TlBr$	0.0113	0.62	6.1×10^2
$(p$-$HC_6F_4)_2TlBr$	0.0213	0.56	1.6×10^3
$(C_6F_5)_2TlCl$	0.0116	0.53	1.5×10^4
$(p$-$HC_6F_4)_2TlCl$	0.0136	0.54	4.7×10^3

[a] Expressed in terms of R_2TlX monomers. [b] i = calcd. mol. wt. for the monomer/observed mol. wt.

[c] $K_{dim} = \dfrac{1-i}{\text{concn.}\,(2i-1)^2}$ is the equilibrium constant for reaction 1.

TABLE 3

MOLECULAR WEIGHT DATA AND EQUILIBRIUM CONSTANTS FOR HALOGENOBIS(POLYFLUOROPHENYL)(TRIPHENYLPHOSPHINE OXIDE)THALLIUM(III) COMPOUNDS IN SOLUTION

Compound	In acetone			In benzene		
	Concn. [a] (mol dm^{-3})	i [b]	K [c] (mol^{-1} dm^{3})	Concn. [a] (mol dm^{-3})	i [b]	K_{dim} [d] (mol^{-1} dm^{3})
$(C_6F_5)_2Ph_3POTlBr$	0.0133	1.56	106	0.0148	0.95	3.8
	0.0221	1.48	99	0.0245	0.94	3.2
(p-$HC_6H_4)_2Ph_3POTlBr$	0.0139	1.65	60	0.0154	0.97	1.9
	0.0232	1.57	56	0.0257	0.96	1.7
(o-$HC_6F_4)_2Ph_3POTlBr$	0.0140	1.62	70	0.0154	0.90	11
	0.0230	1.52	75	0.0255	0.86	10
$(C_6F_5)_2Ph_3POTlCl$	0.0140	1.55	107	0.0080	0.90	20
	0.0233	1.47	102			
(p-$HC_6F_4)_2Ph_3POTlCl$	0.0146	1.62	66	[e]		
	0.0243	1.53	71			
(o-$HC_6F_4)_2Ph_3POTlCl$	0.0146	1.59	82	0.0162	0.82	26
	0.0240	1.50	85	0.0272	0.78	25

[a] Expressed in terms of R_2Ph_3POTlX monomers. [b] i = calcd. monomeric mol. wt./observed mol. wt.
[c] $K = (2 - i)/(\text{concn.})(i - 1)^2$, is the equilibrium constant for the reaction, $R_2TlX + Ph_3PO \rightleftharpoons R_2Ph_3POTlX$ [reverse of reaction 3]. [a] $K_{dim} = (1 - i)/(\text{concn.})(2i - 1)^2$, is the equilibrium constant for reaction 4.
[e] Solubility <0.01 mol dm^{-3}.

molecules/molecule of (p-$HC_6F_4)_2TlBr$], and this was only slowly removed by heating under vacuum. Accordingly, reaction 2 occurs on dissolution of R_2TlX derivatives in acetone.

$$(R_2TlX)_n + xn\ Me_2CO \rightarrow n\ R_2(Me_2CO)_xTlX \qquad (2)$$

The complexes R_2Ph_3POTlX are non-electrolytes in acetone, and the molecular weights in this solvent are less than monomeric values (Experimental Section), indicative of loss of triphenylphosphine oxide.

$$R_2Ph_3POTlX \rightleftharpoons Ph_3PO + R_2TlX \qquad (3)$$

Stability constants for the complexes, calculated from the molecular weight data, are given in Table 3. Molecular weights in benzene slightly but consistently exceed monomeric values, indicative of some dimerization.

$$2\ R_2Ph_3POTlX \rightleftharpoons (R_2Ph_3POTlX)_2 \qquad (4)$$

This was not observed in previous studies of $(C_6F_5)_2Ph_3POTlX$ complexes [3]. Equilibrium constants for reaction (4) are given in Table 3.

The complexes R_2 bpyTlX are appreciably dissociated in acetone, as indicated by i (monomer formula wt./observed mol.wt.) values of 1.11—1.44 (Table 4). Although the conductances in this solvent are significant (Table 4) they are generally too small for the ionization reaction 5 (L = bpy) to account for most of the dissociation *.

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* Molar conductances of 1 : 1 electrolytes in acetone are 90—160 S cm^2 mol^{-1} [16].

TABLE 4

MOLECULAR WEIGHT AND CONDUCTANCE DATA FOR 2,2′-BIPYRIDYLHALOGENOBIS(POLYFLUOROPHENYL)THALLIUM(III) COMPOUNDS IN ACETONE

Compound	Concn.[a] (mol dm^{-3})	i[b]	Mol. cond. (S cm^2 mol^{-1})	Compound	Concn.[a] (mol dm^{-3})	i[b]	Mol. cond. (S cm^2 mol^{-1})
$(C_6F_5)_2$bpyTlBr	0.00139		22.6	$(C_6F_5)_2$bpyTlCl	0.00095		15.8
	0.0121		14.1		0.0135		9.7
	0.0154	1.12			0.0163	1.16	
	0.0254	1.18			0.0268	1.11	
$(p\text{-}HC_6F_4)_2$bpyTlBr	0.00198		21.5	$(p\text{-}HC_6F_4)_2$bpyTlCl	0.00270[c]		12.3
	0.00872		15.4				
	0.0101	1.25					
$(o\text{-}HC_6F_4)_2$bpyTlBr	0.00186		16.0	$(o\text{-}HC_6F_4)_2$bpyTlCl	0.00212		12.2
	0.00316		16.8		0.0130		9.4
	0.00611		19.3		0.0171	1.43	
	0.0118		18.1		0.0244	1.36	
	0.0162	1.44					
	0.0207	1.40					

[a] Expressed in terms of R_2bpyTlX monomers. [b] i = calcd. monomeric mol. wt./observed mol. wt. [c] Concn. limit.

$$R_2LTlX \rightleftharpoons R_2LTl^+ + X^- \tag{5}$$

Moreover, there is no clear relationship between the magnitude of *i* and the molar conductance. Thus, loss of 2,2′-bipyridyl (reaction 6; L = bpy) must occur,

$$R_2LTlX \rightleftharpoons R_2TlX + L \tag{6}$$

as has previously been observed for $(C_6F_5)_2bpyTlO_2CR$ complexes [17]. Two features of the conductance data are not readily explicable if ionization arises from reaction 5, viz. the near concentration independence of the molar conductances of $(o\text{-}HC_6F_4)_2bpyTlBr$, and the much greater conductances for $(C_6F_5)_2$-bptTlX complexes (Table 4) than the corresponding 1,10-phenanthroline (phen) derivatives (mol. cond., 1.5—4.5 S cm^2 mol^{-1}) [2]. Since $(C_6F_5)_2phenTlX$ complexes are more stable than their 2,2′-bipyridyl analogues with respect to loss of the uncharged ligand (reaction 6), e.g. when X = Br or Cl (compare present data (Table 4) with that of ref. 2) or X = RCO_2 [17], this might have been expected to promote greater ionization (reaction 5) when L = phen than when L = bpy.

An alternative explanation to reaction 5 for the conductivities of the 2,2′-bipyridyl complexes is provided by reaction 7 (L = bpy), in which R_2TlX species produced by the dissociation reaction 6 react with the parent complex.

$$R_2LTlX + R_2TlX \rightleftharpoons R_2LTl^+ + R_2TlX_2^- \tag{7}$$

The specific conductivities of 1 : 1 mixtures of $R_2bpyTlBr$ and R_2TlBr derivatives in acetone are much greater than the sum of the specific conductivities of the individual compounds (Table 5), consistent with the occurrence of reaction 7. Similar evidence for this reaction when R = C_6F_5, L = phen, and X = Br has been reported [2]. Since ionization by reaction 7 is dependent on formation of the appropriate R_2TlX species by reaction 6, the lack of dissociation of $(C_6F_5)_2phenTlX$ complexes by reaction 6 accounts for their low conductances. With reactions 6 and 7 as the dissociation paths, the conductivity of any $R_2bpyTlX$ complex should reach a maximum at a mole ratio $R_2bpyTlX : R_2TlX$ = 1 : 1 [i = 1.5, see reaction 6], since this corresponds to the stoichiometry of reaction 7. As this ratio approaches ∞ [i = 1.0, see reaction 6] at high concentrations or 0 [i = 2.0] at low concentrations, the conductivity should decrease to 0. In the case of $(o\text{-}HC_6F_4)_2bpyTlBr$, *i* values of ca. 1.4 have been observed (Table 4). At the lower concentrations used for conductance measurements, *i* is presumably larger, though molecular weights could not be measured. If these values lie

TABLE 5

SPECIFIC CONDUCTIVITIES OF ACETONE SOLUTIONS CONTAINING EQUIMOLAR AMOUNTS OF $R_2bpyTlBr$ AND R_2TlBr

R	Concn. [a] (mol dm^{-3})	Found, $10^6\ K_{sp}$ (S cm^{-1})	Calc. $10^6\ K_{sp}$ [b] (S cm^{-1})
C_6F_5	0.00139	285	ca. 150
$p\text{-}HC_6F_4$	0.00198	385	ca. 195
$o\text{-}HC_6F_4$	0.00158	219	ca. 155

[a] Of each reagent. [b] Assuming conductivities of the reactants are additive.

TABLE 6

MOLECULAR WEIGHT DATA AND EQUILIBRIUM CONSTANTS FOR 2,2′-BIPYRIDYLHALOGENOBIS(PENTAFLUOROPHENYL)THALLIUM(III) COMPOUNDS IN BENZENE

Compound	Concn. [a] (mol dm^{-3})	i [b]	K_{dim} [c] (mol^{-1} dm^3)
$(C_6F_5)_2$bpyTlBr	0.0171	0.93	5.1
	0.0283	0.89	6.3
$(C_6F_5)_2$bpyTlCl	0.0178	0.86	16
	0.0300	0.80	20

[a] Expressed in terms of $(C_6F_5)_2$bpyTlX monomers. [b] i = calc. mol. wt. for the monomer/observed mol. wt. [c] $K_{dim} = \frac{1-i}{\text{Concn.}\,(2i-1)^2}$, is the equilibrium constant for reaction 8.

in the range $i = 1.4$—1.6, then all the corresponding conductance values would be close to the maximum and hence relatively insensitive to changes in concentration, as observed (Table 4).

Molecular weights of $(C_6F_5)_2$bpyTlX complexes in benzene (p-HC_6F_4 and o-HC_6F_4 derivatives are insufficiently soluble) are significantly higher than monomeric values, indicative of reaction 8 ($R = C_6F_5$), for which equilibrium constants are given in Table 6.

$$2\ R_2\text{bpyTlX} \rightleftharpoons (R_2\text{bpyTlX})_2 \qquad (8)$$

Deviation from the monomeric value is apparent in one earlier measurement for $(C_6F_5)_2$bpyTlBr, but was overlooked in drawing structural conclusions [2].

Molecular weights of $(C_6F_5)_2Ph_3PTlBr$ and 1 : 1 mixtures of triphenylphosphine and R_2TlBr derivatives ($R = p$-HC_6F_4 or o-HC_6F_4) in acetone are considerably less than the calculated values for the appropriate R_2Ph_3PTlBr complexes, indicative of substantial dissociation (reaction 9).

$$R_2Ph_3PTlBr \rightleftharpoons R_2TlBr + Ph_3P \qquad (9)$$

Stability constants for formation of the triphenylphosphine complexes are given in Table 7.

TABLE 7

MOLECULAR WEIGHT DATA AND EQUILIBRIUM CONSTANTS FOR BROMOBIS(POLYFLUOROPHENYL)TRIPHENYLPHOSPHINETHALLIUM(III) COMPLEXES IN ACETONE

Compound	Concn. [a] (mol dm^{-3})	i [b]	K [c] (mol^{-1} dm^3)
$(C_6F_5)_2Ph_3PTlBr$	0.0134	1.76	31
	0.0224	1.71	25
$(p$-$HC_6F_4)_2Ph_3PTlBr$ [d]	0.0141	1.78	26
	0.0235	1.73	21
$(o$-$HC_6F_4)_2Ph_3PTlBr$ [d]	0.0141	1.94	4.6
	0.0235	1.96	1.9

[a] Expressed in terms of R_2TlX monomers. [b] Calc. monomeric mol. wt./observed mol. wt. [c] Equilibrium for the reaction $R_2TlBr + Ph_3P \rightleftharpoons R_2Ph_3PTlBr$, given by $K = (2 - i)/(\text{concn.})(i - 1)^2$. [d] 1 : 1 mole ratio mixture of R_2TlBr and Ph_3P used.

4. *The influence of the aryl group on the coordination chemistry*

The formation of the complexes R_2LTlX (L = bpy or Ph_3PO; X = Br or Cl) when R = C_6F_5, *p*-HC_6F_4, or *o*-HC_6F_4 (section 1) but not when R = Ph or *p*-MeC_6H_4 [18] may be attributed to the electron withdrawing character of the polyfluoroaryl ligands [19], though the low solubilities of the diphenyl- and di-*p*-tolyl-thallium(III) halides must also be a contributing factor. Relative electronegativities may also account for the much higher ν(Tl—X) frequencies for R_2TlX (R = C_6F_5, *p*-HC_6F_4, or *o*-HC_6F_4) (Table 1) than for the corresponding diphenylthallium(III) halides [ν(Tl—Cl), ca. 126 cm^{-1}; ν(Tl—Br), 97 cm^{-1} [20]]. The differences in behaviour between the polyfluoroaryl groups do not conform to a simple pattern. Preparative evidence, e.g. isolation of $(p\text{-}HC_6F_4)_2(Me_2CO)$-TlBr, tenacious hydration of $(p\text{-}HC_6F_4)_2TlCl$, formation of $(p\text{-}HC_6F_4)_2$-$(Ph_3PO)_{1.2}TlBr$ under conditions giving $R_2Ph_3POTlBr$ (R = C_6F_5 or *o*-HC_6F_4), and problems in isolation of $(o\text{-}HC_6F_4)_2Ph_3POTlCl$ (section 1), suggest that coordination of oxydonor ligands is favoured by *p*-HC_6F_4 > C_6F_5 > *o*-HC_6F_4. However, the stability constants for formation of the triphenylphosphine oxide complexes R_2Ph_3POTlX in acetone (Table 3) lie in the sequence R = C_6F_5 (1.6)> *o*-HC_6F_4(1.2) > *p*-HC_6F_4(1.0) for both X = Br and Cl. The lack of differentiation between the polyfluorophenyl groups and the change in sequence from that indicated by the preparative results may arise because the stability constants refer to a reaction involving competition between coordination by two oxydonor ligands.

$$R_2(Me_2CO)TlX + Ph_3PO \rightleftharpoons R_2Ph_3POTlX + Me_2CO$$

If, as preparative results suggest, coordination of acetone to $(p\text{-}HC_6F_4)_2TlX$ derivatives is strong, then this could account for the low relative stabilities of $(p\text{-}HC_6F_4)_2Ph_3POTlX$ complexes in acetone.

A different stability sequence with greater differentiation between the effects of the polyfluoroaryl groups is observed for R_2Ph_3PTlBr (R = C_6F_5, *p*-HC_6F_4 or *o*-HC_6F_4) complexes in acetone, viz. R = C_6F_5 (7) > *p*-HC_6F_4(6) > *o*-HC_6F_4(1). Again, relative stabilities for the R_2TlX : Me_2CO interaction may determine the relative positions of C_6F_5 and *p*-HC_6F_4. The values of *i* for $R_2bpyTlX$ complexes in acetone (Table 4) suggest that dissociation in this solvent follows the same order as for the triphenylphosphine complexes. Stability constants for loss of 2,2′-bipyridyl were not calculated, since ionization is significant (Table 4 and section 3). Use of benzene, which is less polar and hence less strongly coordinated to thallium than acetone, is unsuitable for studying interactions of R_2TlX compounds with uncharged ligands (L) owing to dimerization of both R_2TlX and R_2LTlX complexes in this medium (section 3).

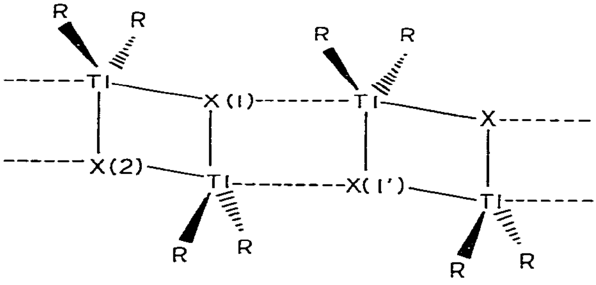
The generally weaker acceptor character when R = *o*-HC_6F_4 than when R = C_6F_5 or *p*-HC_6F_4 is readily attributable to the absence of the strong electron-withdrawing effect of a second fluorine *ortho* to thallium. The ambivalence in the relative effects of C_6F_5 and *p*-HC_6F_4 may be associated with a fine balance between the —I and +R effects of a fluorine *para* to thallium.

The relative effects of the polyfluoroaryl groups on the dimerization reactions 1, 4, and 8 have not been conclusively ascertained, as the molecular weight data are incomplete owing to solubility limitations (Tables 2, 3, and 6).

There is evidence that dimerization of R_2Ph_3POTlX species (reaction 4) is greatest when R = o-HC_6F_4 (Table 3). By contrast, ν(Tl—X) frequencies (Table 1) suggest that thallium—halogen bonding is stronger when R = C_6F_5 or p-HC_6F_4 than when R = o-HC_6F_4. The discrepancy is resolvable if the $(R_2Ph_3POTlX)_2$ species have unsymmetrical halogen bridging, as established when R = C_6F_5 or p-HC_6F_4; X = Br or Cl (section 5). The ν(Tl—X) modes may predominantly involve stretching of the shorter Tl—X bonds, which are presumably stronger for R = C_6F_5 or p-HC_6F_4 than for R = o-HC_6F_4, whereas the extent of dimerization reflects the strength of the weaker Tl—X bridges. These may be stronger for R = o-HC_6F_4, if the dimer is more symmetrical in this case (see also section 5b).

5. *Structures of the complexes*

a. R_2TlX derivatives. The recently determined structure of bromobis(2,3,5,6-tetrafluorophenyl)thallium(III) has shown it to be polymeric with unsymmetrical bromine bridging (A; R = p-HC_6F_4; X = Br) [9]. Similar structures are likely for R_2TlBr (R = C_6F_5 or o-HC_6F_4), since their metal—halogen vibrational frequencies are similar to those of $(p\text{-}HC_6F_4)_2TlBr$ (Table 1), and for $(C_6F_5)_2$-$TlCl$ which is isomorphous with the corresponding bromide (section 2).



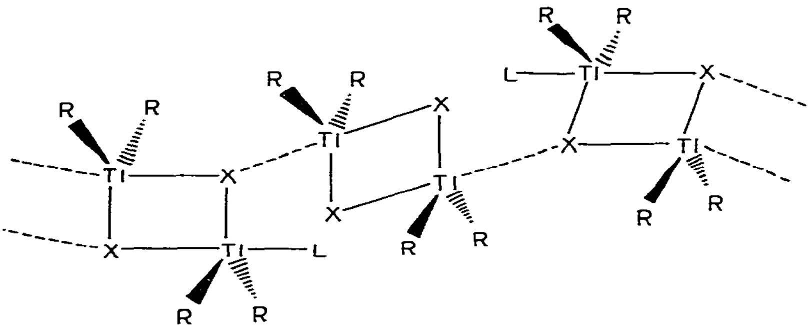
(A)

R = p—HC_6F_4 or o—C_6F_4 , X = Br; R = C_6F_5 , X = Br or Cl

when R = p—HC_6F_4., X = Br; Tl—Br(1), 2.734 Å; Tl—Br(2), 3.016 Å

TlBr(1'), 3.214 Å

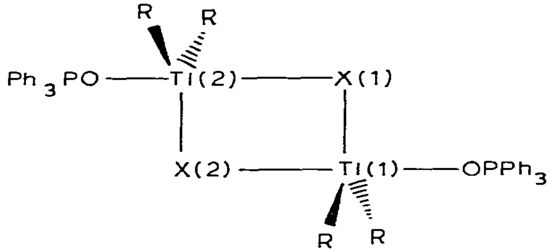
The slight hydration of $(p\text{-}HC_6F_4)_2TlCl$ presumably accounts for the lack of isomorphism with $(p\text{-}HC_6F_4)_2TlBr$. Nevertheless, the structures may be closely related. For example, coordination of water could cause partial disruption of the halogen bridging of A without greatly changing the structure, e.g. B (R = p-HC_6F_4; X = Cl; L = H_2O). It may be significant that, despite hydration, ν(Tl—Cl) of $(p\text{-}HC_6F_4)_2TlCl$ is similar to that of $(C_6F_5)_2TlCl$ (Table 1), which has structure A. The isolated location of the water molecules in B can be correlated with the lack of hydrogen-bonding in the hydrate (section 1). The dimeric nature of R_2TlX (R = C_6F_5 or p-HC_6F_4; X = Br or Cl) derivatives in benzene is readily explicable in terms of cleavage of the weakest thallium—halogen bonds in A (or B). From molecular weight data in acetone (section 3), $(o\text{-}HC_6F_4)_2TlCl$ has an associated structure. Since it is less soluble in benzene than the polymeric complexes A, some form of polymeric chlorine-bridged



(B)

structure can be inferred. Uncertainty in the assignment of ν(Tl—Cl) (Table 1) rules out use of thallium—halogen vibrational frequencies in further structural speculation.

b. R_2Ph_3POTlX derivatives. X-ray crystallography has shown (p-$HC_6F_4)_2$-$Ph_3POTlCl$ to be a halogen-bridged dimer C (R = p-HC_6F_4; X = Cl), and isomorphous relationships (section 2) and/or similarity of thallium—halogen frequencies (Table 1) has enabled the structure also to be assigned to (p-$HC_6F_4)_2Ph_3POTlBr$ and $(C_6F_5)_2Ph_3POTlX$ (X = Br or Cl) [8]. Although



For R = p—HC_6F_4 ; X = Cl

Tl(1)—Cl(1) = Tl(2)—Cl(2) , 2.541 Å

Tl(1)—Cl(2) = Tl(2)—Cl(1) , 2.936 Å

(C)

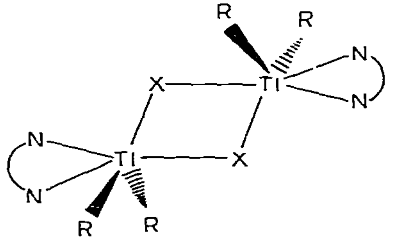
R = p—HC_6F_4 or C_6F_5 ; X = Br or Cl

the thallium—halogen frequencies of (o-$HC_6F_4)_2Ph_3POTlX$ complexes are somewhat less than those of their pentafluorophenyl and 2,3,5,6-tetrafluorophenyl counterparts, the lowering seems less than would be expected for a gross change of structure. Possibly, the complexes have a more symmetrical dimeric arrangement than C, the shorter thallium—halogen bonds being longer than in the complexes with structure C. In addition, the longer thallium—halogen bonds may be shorter in (o-$HC_6F_4)_2Ph_3POTlX$ than in C (section 4). There is a close relationship between structures A and C. The latter can be derived from the former by replacement of alternate pairs (the weakest) of halogen bridges by triphenylphosphine oxide.

Previous X-ray powder data, together with the similarity in ν(Tl—Cl) frequencies for $(C_6F_5)_2Ph_3AsOTlCl$ [3] and $(C_6F_5)_2Ph_3POTlCl$ (Table 1), suggest that the complexes $(C_6F_5)_2Ph_3AsOTlX$ (X = Br or Cl) have a structure similar to C. The structural similarity may also extend to the isomorphous complexes $(C_6F_5)_2LTlX$ (L = Ph_3P or Ph_3As), since ν(Tl—Cl) frequencies of the chloro complexes [3] are near that of $(C_6F_5)_2Ph_3POTlCl$.

c. Non-stoichiometric triphenylphosphine oxide complexes. Phosphorus—oxygen stretching frequencies indicate that (o-HC_6F_4)$_2$(Ph_3PO)$_{0.35}$TlCl contains a complex species different from (o-HC_6F_4)$_2Ph_3$POTlCl (section 1). A polymer with the arrangement B (R = o-HC_6F_4; X = Cl; L = Ph_3PO) as the repeating unit would have the composition (o-HC_6F_4)$_2$(Ph_3PO)$_{0.33}$TlCl. Structure B is intermediate between the double halogen-bridged polymer A and the dimer C. Another possibility is a structure in which some of the weaker halogen bridges of A are replaced by bridging phosphine oxide ligands. At this stage, these alternatives cannot be distinguished. The ν(PO) frequencies of the solid (o-HC_6F_4)$_2$ (Ph_3PO)$_{0.55}$TlCl (section 1) are readily explicable if the product is a mixture of (o-HC_6F_4)$_2Ph_3$POTlCl [ν(PO), 1162 cm^{-1}] and the species present in (o-HC_6F_4)$_2$ (Ph_3PO)$_{0.35}$TlCl [ν(PO), 1131 cm^{-1}]. Although it was not possible to support the hypothesis that (p-HC_6F_4)$_2$(Ph_3PO)$_{1.2}$TlBr contains (p-HC_6F_4)$_2$ (Ph_3PO)$_2$TlBr by an independent synthesis of the latter, there have been two analogous complexes prepared previously, viz. (C_6F_5)$_2L_2TlNO_3$ (L = Ph_3PO or Ph_3AsO) [3]. However, the structure proposed for these compounds, monomeric with trigonal bipyramidal thallium and a linear CTlC arrangement [3], is inconsistent with the observation of non-linear CTlC groups in all bis-(polyfluorophenyl)thallium(III) compounds of crystallographically established structure viz. (C_6F_5)$_2$TlOH [6], (C_6F_5)$_2$Tldpa (dpa = 2,2'-dipyridylamide) [21], (p-HC_6F_4)$_2$ TlBr [9], and (p-HC_6F_4)$_2$ Ph_3POTlCl [8]. It is more likely that the phosphine or arsine oxide ligands are axial and two carbons and nitrate are equatorial.

d. R_2 bpyTlX complexes. Reinvestigation of the molecular weights of (C_6F_5)$_2$ bpyTlX (X = Cl or Br) derivatives has revealed significant association in benzene (Table 6), by contrast with an earlier conclusion [2] that they are monomeric in this solvent. Equilibrium constants (Table 6) for dimer formation are similar to those (Table 3) of R_2Ph_3POTlX complexes, which are dimeric (C) in the solid state. Thus, a dimeric structure (D) is likely, rather than the five coordinate monomer previously proposed [2].



(D)

For (C_6F_5)$_2$ bpyTlBr, ν(Tl—Br) is coincident in the infrared and Raman (Table 1), and this is also possible for the chloro complex, although the assignments are less certain. Thus, the halogen bridging is probably unsymmetrical, as observed for R_2Ph_3POTlX complexes (section 5b), and the vibration assigned to ν(Tl—X) involves predominantly stretching of the short bridging Tl—X bond. Assignments of ν(Tl—X) for (p-HC_6F_4)$_2$ bpyTlX are less clear, but appear similar to those of the pentafluorophenyl analogues suggesting a similar structure. On the other hand, the ν(Tl—X) frequencies of (o-HC_6F_4)$_2$ bpyTlX complexes are lower than those of the C_6F_5 and p-HC_6F_4 derivatives, and the Raman and infrared values are not coincident. These observations can be rationalised in terms of a weaker, more symmetrically bridged dimer.

It is also likely that $(C_6F_5)_2$phenTlX (phen = 1,10-phenanthroline; X = Br or Cl) complexes have the dimeric structure D. The reported molecular weight data [2] provide evidence for slight association in benzene, the significance of which was previously overlooked.

e. Summary and conclusions. Thus, halogenobis(polyfluorophenyl)thallium(III) complexes show greater association and higher coordination numbers than were originally proposed [2—4] for the pentafluorophenyl derivatives. In particular the complexes R_2TlX, R_2Ph_3POTlX, and R_2bpyTlX are not four coordinate dimers, four coordinate monomers, and five coordinate monomers, respectively, as reported for R = C_6F_5; X = Br or Cl [2—4], but are five coordinate polymers, five coordinate dimers, and six coordinate dimers, respectively, when R = C_6F_5 or p-HC_6F_4. Unsymmetrical TlXTl bridging and non-linear CTlC arrangements are established or highly likely in all cases. These results have led to reinterpretation of reported molecular weight and infrared data [2,3] for other $(C_6F_5)_2$LTlX (X = Br or Cl) complexes, and the compounds are now considered to be dimeric with halogen bridging and five (L = Ph_3AsO, Ph_3P or Ph_3As) or six (L = phen) coordinate thallium. The revised structures for the bis(polyfluorophenyl)thallium(III) compounds provide a ν(Tl—X)/coordination number correlation in satisfactory agreement with that for inorganic halogenothallium(III) complexes [22] by contrast with earlier proposals [2—4] for $(C_6F_5)_2Tl$ compounds. On this basis, the ν(Tl—Cl) frequencies for $(C_6F_5)_2TlCl_2^-$ (265—230 cm^{-1}) appear too low to sustain the reported tetrahedral stereochemistry [2] (cf. $TlCl_4^-$ [22], ca. 300 cm^{-1}), and an associated arrangement with ClTlCl bridging and a higher coordination number for thallium is likely.

The situation is more complex for 2,3,4,5-tetrafluorophenylthallium(III) complexes. The structure of $(o$-$HC_6F_4)_2TlBr$ is similar to that of R_2TlBr (R = C_6F_5 or p-HC_6F_4). For the other compounds, the coordination number may be the same as in the C_6F_5 or p-HC_6F_4 analogues, but the halogen bridging is probably more symmetrical.

Experimental

1. *General*

Microanalyses (C, H, F) were by the Australian Microanalytical Service, Melbourne. Bromine and chlorine analyses refer to ionizable halide, which was determined by potentiometric titration of the compounds in acetone with aqueous silver nitrate. Molecular weights in acetone and in benzene were measured at 25° C with Hewlett-Packard 302 and 301A vapour pressure osmometers. Concentrations are given in parentheses as %w/w. Molar conductances (S cm^2 mol^{-1}) were obtained from measurements in acetone at 20—25°C. A Wayne-Kerr B221 Universal bridge and a conventional cell fitted with shiny platinum electrodes were used; concentrations (mol dm^{-3}) are given in parentheses. Values for known compounds are consistent with reported values [2,3]. NMR spectra were obtained with Varian A56/60A and Bruker WH90 instruments. Proton chemical shifts are in ppm downfield from internal tetramethylsilane, and fluorine chemical shifts are in ppm upfield from internal $CFCl_3$. Infrared spectra (3800—50 cm^{-1}) of compounds as Nujol and hexachlorobutadiene mulls were recorded with a Perkin-Elmer 180 spectrophotometer. Lists of absorption frequencies are available from the authors. The spectra of R_2TlBr (R = C_6F_5, p-HC_6F_4, or o-HC_6F_4), $(C_6F_5)_2TlCl$, $(C_6F_5)_2Ph_3POTlX$, $(C_6F_5)_2$bpyTlX (X = Br or Cl), and $(C_6F_5)_2Ph_3PTlBr$ complexes were in satisfactory agreement with reported data [1—4,7,14,23]. Raman spectra of solid bipyridyl complexes were recorded with a Spex Ramalog 5 (14018 Double monochromator) instrument. Details for the region 500—100 cm^{-1} can be obtained from the authors. X-ray powder data were obtained with a Philips X-ray diffractometer PW 1050/25 wide angle goniometer or a Philips Debye-Sherrer 114.6 mm powder camera. Nickel filtered Cu-K_α radiation was used in each case.

2. *Solvents and reagents*

Univar acetone and May and Baker 'Pronalys' benzene were used for conductivity and molecular weight determinations. Ether and benzene for preparative work were distilled from calcium hydride and stored over sodium. Other solvents were of reagent grade quality. Triphenylphosphine (Ega) was recrystallized from absolute ethanol and was free (IR criterion) from triphenylphosphine oxide. Triphenylphosphine oxide was prepared by a reported method [24] and was recrystallized twice from benzene. 2,2′-Bipyridyl (Hopkins and Williams) was recrystallized from petroleum (b.p. 60—70° C).

3. *Halogenobis(polyfluorophenyl)thallium(III) compounds*

The compounds R_2TlBr (R = C_6F_5, p-HC_6F_4 or o-HC_6F_4) were prepared by the reported methods [2,7,10] and had spectroscopic data consistent with literature values [2,4,7,23,25], whilst the derivatives R_2TlCl (R = C_6F_5, p-HC_6F_4 or o-HC_6F_4) were prepared by the method for $(C_6F_5)_2TlCl$ [2].

Bromobis(pentafluorophenyl)thallium(III). m.p. 224—228° C, lit. [2], m.p. 217—220° C (Found: mol. wt. (in acetone), 616 (1.50%); 610 (2.53%); (in benzene), 1001 (0.80%) $C_{12}BrF_{10}Tl$ calcd.: mol. wt., 618). Mol. cond., 1.9 (2.51 × 10^{-3}).

Bromobis(2,3,5,6-tetrafluorophenyl)thallium(III). m.p. 250—254° C, lit. [7], m.p. 237—240° C (dec.) (Found: mol. wt. (in acetone), 583 (1.50%); 579 (2.43%); (in benzene), 1046 (1.42%). $C_{12}H_2BrF_8Tl$ calcd.: mol. wt., 582). Mol. cond., 2.5 (2.92 × 10^{-3}).

Bromobis(2,3,4,5-tetrafluorophenyl)thallium(III). m.p. 257—259° C (dec.), lit. [7], m.p. 271—274°C (dec.) (Found: mol. wt. (in acetone), 588 (1.43%); 590 (2.51%); (in benzene), solubility <0.54%). Mol. cond., 3.9 (2.18 × 10^{-3}).

Chlorobis(pentafluorophenyl)thallium(III). m.p. 249—252° C, lit. [2], m.p. 239—241° C (Found: mol. wt. (in acetone), 587 (1.51%); 578 (2.51%); (in benzene), 1091 (0.76%). $C_{12}ClF_{10}Tl$ calcd.: mol. wt., 574). Mol. cond., 1.3 (2.35 × 10^{-3}). ^{19}F NMR spectrum (acetone-d_6): 119.4 (dd, J(Tl, F) 812 Hz, F2, 6), 152.6 (dt, J(Tl, F) 84 Hz, F4), 160.6 (dt, J(Tl, F) 360 Hz, F3, 5).

Chlorobis(2,3,5,6-tetrafluorophenyl)thallium(III). (nc) Recrystallized from benzene, yield 75%, m.p. 254—256° C (Found: C, 26.7; H, 0.7; Cl, 6.5; F, 28.2; mol. wt. (in acetone), 537 (1.51%); 545 (2.50%); (in benzene), 992 (0.83%). $C_{12}H_2ClF_8Tl$ calcd.: C, 26.8: H, 0.4; Cl, 6.6; F, 28.3%; mol. wt., 538). Mol.

cond., 1.9 (2.53×10^{-3}). ^{19}F NMR spectrum (acetone-d_6): 121.0 (dt, J(Tl, F) 815 Hz, F2, 6), 138.0 (dm, J(Tl, F) 388 Hz, F3, 5).

Infrared absorptions at 3647 and 3570 cm^{-1} were not removed by i) titration of a sample in methanol with dilute hydrochloric acid or ii) treatment of a sample dissolved in benzene with dry HCl gas or iii) treatment with $MgSO_4$ in ether.

Chlorobis(2,3,4,5-tetrafluorophenyl)thallium(III). (nc) Recrystallized from methanol/water, yield 69%, m.p. 303—305°C (dec.) (Found: C, 26.8; H, 0.5; Cl, 6.5; F, 28.6; mol. wt. (in acetone), 561 (1.00%); 582 (2.02%); (in benzene), solubility <0.49%. $C_{12}H_2ClF_8Tl$ calcd.: C, 26.8; H, 0.4; Cl, 6.6; F, 28.3%; mol. wt. 538). Mol. cond., 1.5 (2.44×10^{-3}). ^{19}F NMR spectrum (acetone-d_6): 118.1 (dm, J(Tl, F) 1209 Hz, F2), 138.5 (dm, J(Tl, F) 202 Hz, F5), 154.8 (dm, J(Tl, F) 92 Hz, F4), 155.1 (dt, J(Tl, F) 528 Hz, F3).

4. *Acetone complexes of bromobis(polyfluorophenyl)thallium(III) compounds*

The bromobis(polyfluorophenyl)thallium(III) compound (1.0 g) was dissolved in acetone (5 cm^3) and the solvent was evaporated under a stream of nitrogen to give a white powder. Both $(C_6F_5)_2TlBr$ and $(o\text{-}HC_6F_4)_2TlBr$ were recovered unchanged, whereas the complex $(p\text{-}HC_6F_4)_2Me_2COTlBr$ was obtained from $(p\text{-}HC_6F_4)_2TlBr$.

Acetonebromobis(2,3,5,6-tetrafluorophenyl)thallium(III). (nc) Recrystallized from acetone/petrol (b.p. 60—80°C), yield 65%, m.p. 249—253°C (cf. m.p. of $(p\text{-}HC_6F_4)_2TlBr$ above). (Found: C, 27.9; H, 1.2; Br, 12.5; F, 23.4. $C_{15}H_8BrF_8OTl$ calcd.: C, 28.1; H, 1.3; Br, 12.5; F, 23.7%). The infrared spectrum (3800—650 cm^{-1}) was similar to that of $(p\text{-}HC_6F_4)_2TlBr$ [7], except for an additional strong absorption at 1694 cm^{-1} (Nujol mull of a fresh sample), 1694 and 1678 cm^{-1} (Nujol mull of a week old sample), or 1678 cm^{-1} (hexachlorobutadiene mull of a week old sample). Treatment of the compound with boiling benzene gave $(p\text{-}HC_6F_4)_2(Me_2CO)_{0.4}TlBr$ (Found: Br, 13.2; wt. loss (8 h at 95°C under vacuum), 3.9%. $C_{13.2}H_{4.4}BrF_8O_{0.4}Tl$ calcd.: Br, 13.2; Me_2CO, 3.8%).

5. *Halogenobis(polyfluorophenyl)(triphenylphosphine oxide)thallium(III) compounds*

The complexes R_2Ph_3POTlX ($R = C_6F_5$, X = Br or Cl; $R = o\text{-}HC_6F_4$, X = Br) were prepared as for $(C_6F_5)_2Ph_3POTlBr$ [3]. Preparations of $(p\text{-}HC_6F_4)_2Ph_3POTlX$ (X = Br or Cl) have recently been reported [8]. The compound $(o\text{-}HC_6F_4)_2Ph_3POTlCl$ was prepared by crystallization from a solution of $(o\text{-}HC_6F_4)_2TlCl$ (0.7 mmol) and Ph_3PO (3.5 mmol) in methanol/water.

Bromobis(pentafluorophenyl)(triphenylphosphine oxide)thallium(III). m.p. 202—203°C (dec.), lit. [3], m.p. 199.5—201.5°C (Found: mol. wt. (in acetone), 575 (1.52%); 604 (2.52%); (in benzene), [8]. $C_{30}H_{15}BrF_{10}OPTl$ calcd.: mol. wt., 897). Mol. cond., 2.0 (1.60×10^{-3}).

Bromobis(2,3,5,6-tetrafluorophenyl)(triphenylphosphine oxide)thallium(III). (Found: mol. wt. (in acetone), 522 (1.53%); 547 (2.54%); (in benzene), [8]. $C_{30}H_{17}BrF_8OPTl$ calcd.: mol. wt., 861). Mol. cond., 2.5 (1.61×10^{-3}).

An attempted preparation from methanol/water by the method for $(C_6F_5)_2(Ph_3PO)TlBr$ gave crystals of approximate composition $(p\text{-}HC_6F_4)_2(Ph_3PO)_{1.2}$-

TlBr, m.p. ca. 173—185°C (dec.). (Found: C, 43.5; H, 2.2; Br, 8.6; F, 17.5. $C_{33.6}H_{20}BrF_8O_{1.2}P_{1.2}Tl$ calcd.: C, 44.0; H, 2.2; Br, 8.7; F, 16.6%). None of the crystals floated in carbon tetrachloride (density 1.59 g cm^{-3}; density of Ph_3PO, 1.21 g cm^{-3}). A product of similar stoichiometry (Found: Br, 8.5%) and with the same m.p. and infrared spectrum was obtained upon crystallization from a solution of $(p\text{-}HC_6F_4)_2TlBr$ and Ph_3PO (mole ratio 1 : 2) in methanol/water.

Bromobis(2,3,4,5-tetrafluorophenyl)(triphenylphosphine oxide)thallium(III). (nc) Yield 92%, m.p. 185—187°C (Found: C, 42.1; H, 2.0; Br, 9.3; F, 18.0; mol. wt. (in acetone), 531 (1.53%); 565 (2.52%); (in benzene), 960 (1.52%), 996 (2.51%). $C_{30}H_{17}BrF_8OPTl$ calcd.: C, 41.9; H, 2.0; Br, 9.3; F, 17.7%, mol. wt. 861). Mol. cond., 2.5 (1.56×10^{-3}).

Chlorobis(pentafluorophenyl)(triphenylphosphine oxide)thallium(III). m.p. 221—222°C (dec.), lit. [3], m.p. 216—218°C (Found: mol. wt. (in acetone), 550 (1.52%); 579 (2.53%); (in benzene), [8]. $C_{30}H_{15}ClF_{10}OPTl$ calcd.: mol. wt., 852). Mol. cond., 1.5 (1.75×10^{-3}).

Chlorobis(2,3,5,6-tetrafluorophenyl)(triphenylphosphine oxide)thallium(III). (Found: mol. wt. (in acetone), 503 (1.52%); 535 (2.52%); (in benzene), [8]. $C_{30}H_{17}ClF_8OPTl$ calcd.: mol. wt., 816). Mol. cond., 2.0 (1.75×10^{-3}).

Chlorobis(2,3,4,5-tetrafluorophenyl)(triphenylphosphine oxide)thallium(III). (nc) Yield 95%, m.p. 197—198°C (Found: C, 43.8; H, 2.4; Cl, 4.4; F, 18.2; mol. wt. (in acetone), 514 (1.52%); 545 (2.49%); (in benzene), 993 (1.52%); 1044 (2.54%). $C_{30}H_{17}ClF_8OPTl$ calcd.: C, 44.1; H, 2.1; Cl, 4.3; F, 18.6%; mol. wt., 816). Mol. cond., 1.8 (1.75×10^{-3}).

An attempted preparation by crystallization from a methanol/water solution containing equimolar amounts of $(o\text{-}HC_6F_4)_2TlCl$ and Ph_3PO gave a white, crystalline product of approximate composition $(o\text{-}HC_6F_4)_2(Ph_3PO)_{0.35}TlCl$, softens 185—188°C, not completely melted at 260°C (Found: C, 33.8; H, 1.3; Cl, 5.5. $C_{18.3}H_{7.25}ClF_8O_{0.35}P_{0.35}Tl$ calcd.: C, 34.6; H, 1.2; Cl, 5.6%). A similar preparation with a twofold excess of Ph_3PO gave a product of composition $(o\text{-}HC_6F_4)_2(Ph_3PO)_{0.55}TlCl$, softens 183—185°C, m.p. 185—230°C (Found: Cl, 5.1. $C_{21.9}H_{10.3}ClF_8O_{0.55}P_{0.55}Tl$ calcd.: Cl, 5.1%).

6. *2,2'-Bipyridylhalogenobis(polyfluorophenyl)thallium(III) compounds*

The complexes $R_2bpyTlX$ ($R = C_6F_5$ or $o\text{-}HC_6F_4$; X = Br or Cl) were prepared by crystallization from a solution containing equimolar amounts of the R_2TlX compound and 2,2'-bipyridyl in methanol/water. Precipitation of $(p\text{-}HC_6F_4)_2bpyTlX$ complexes occurred on mixing solutions of $(p\text{-}HC_6F_4)_2TlX$ and 2,2'-bipyridyl (mole ratio, 1 : 1) in ether. Conductances are given in Table 4.

2,2'-Bipyridylbromobis(pentafluorophenyl)thallium(III). Yield 92%, m.p. 174—176°C, lit. [2], m.p. 171.5—172.5°C (Found: Br, 10.3; mol. wt. (in acetone), 640 (1.52%); 659 (2.51%); (in benzene), 829 (1.52%); 870 (2.51%). $C_{22}H_8BrF_{10}N_2Tl$ calcd.: Br, 10.3%; mol. wt., 775).

2,2'-Bipyridylbromobis(2,3,5,6-tetrafluorophenyl)thallium(III). (nc) Yield 99%, m.p. 267—268°C (dec.) (Found: C, 35.8; H, 1.5; Br, 10.8; F, 20.2; mol. wt. (in acetone), 561 (0.74%); 591 (0.95%); (in benzene), solubility <0.60%. $C_{22}H_{10}BrF_8N_2Tl$ calcd.: C, 35.8; H, 1.4; Br, 10.8; F, 20.6%; mol. wt., 739).

2,2'-Bipyridylbromobis(2,3,4,5-tetrafluorophenyl)thallium(III). (nc) Yield

91%, m.p. 177—180° C (Found: C, 35.5; H, 1.4; Br, 10.8; F, 20.5; mol. wt. (in acetone), 512 (1.52%); 528 (2.51%); (in benzene), solubility <0.58%. $C_{22}H_{10}BrF_8N_2Tl$ calcd.: C, 35.8; H, 1.4; Br, 10.8; F, 20.6%; mol. wt. 739).

2,2'-Bipyridylchlorobis(pentafluorophenyl)thallium(III). Yield 89%, m.p. 160—166° C (single crystal, 167—168° C), lit. [2], m.p. 167.5° C (Found: C, 35.5; H, 1.1; Cl, 4.9; mol. wt. (in acetone), 629 (1.52%); 657 (2.49%); (in benzene), 852 (1.49%); 918 (2.50%). $C_{22}H_8ClF_{10}N_2Tl$ calcd.: C, 36.2; H, 1.1; Cl, 4.9%; mol. wt. 730).

2,2'-Bipyridylchlorobis(2,3,5,6-tetrafluorophenyl)thallium(III). (nc) Yield 99%; m.p. 275—277°C (dec.) (Found: C, 38.3; H, 1.5; Cl, 5.1; F, 21.5; mol. wt. (in acetone), solubility <0.63%; (in benzene), solubility <0.47%. $C_{22}H_{10}ClF_8N_2Tl$ calcd.: C, 38.1; H, 1.5; Cl, 5.1; F, 21.9%; mol. wt. 694).

2,2'-Bipyridylchlorobis(2,3,4,5-tetrafluorophenyl)thallium(III). (nc) Yield 95%, m.p. 199—201°C (dec.) (Found: C, 37.9; H, 1.6; Cl, 5.2; F, 21.8%; mol. wt. (in acetone), 486 (1.51%); 512 (2.16%); (in benzene), solubility <0.52%. $C_{22}H_{10}ClF_8N_2Tl$ calcd.: C, 38.1; H, 1.5; Cl, 5.1; F, 21.9%; mol. wt. 694).

7. *Bromobis(polyfluorophenyl)(triphenylphosphine)thallium(III) compounds*

Bromobis(pentafluorophenyl)(triphenylphosphine)thallium(III). The complex was prepared by crystallization from a solution containing stoichiometric amounts of $(C_6F_5)_2TlBr$ and Ph_3P in methanol/water, yield 87%, m.p. 135—137°C (dec.), lit. [3], dec. 140—160°C (Found: C, 40.9; H, 1.9; F, 21.5%; mol. wt. (in acetone), 500 (1.50%); 514 (2.51%). $C_{30}H_{15}BrF_{10}PTl$ calcd.: C, 40.9; H, 1.7; F, 21.6%; mol. wt., 881).

Attempted preparations of $(p\text{-}HC_6F_4)_2(Ph_3P)TlBr$ and $(o\text{-}HC_6F_4)_2(Ph_3P)TlBr$ by a similar method gave crystalline products of approximate composition $R_2(Ph_3P)_{1.4}TlBr$ ($R = p\text{-}HC_6F_4$ or $o\text{-}HC_6F_4$) (Found: C, 47.5% ($R = p\text{-}HC_6F_4$), C, 46.0% ($R = o\text{-}HC_6F_4$). $C_{37.2}H_{23}BrF_8P_{1.4}Tl$ calcd.: C, 47.1%). Molecular weight measurements in acetone: (i) $(p\text{-}HC_6F_4)_2TlBr$ and Ph_3P (mole ratio 1 : 1) Found: 475 (1.52%); 487 (2.52%). $(p\text{-}HC_6F_4)_2Ph_3PTlBr$ ($C_{30}H_{17}BrF_8PTl$) calcd.: mol. wt., 845. (ii) $(o\text{-}HC_6F_4)_2TlBr$ and Ph_3P (mole ratio, 1 : 1) Found: 435 (1.52%); 431 (2.53%). $(o\text{-}HC_6F_4)_2Ph_3PTlBr$($C_{30}H_{17}BrF_8PTl$) calcd.: mol. wt. 845.

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